Handbook of instrumental techniques from CCiTUB

Advanced applications of Scanning Electron Microscopy in Geology

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Abstract. Nowadays Scanning Electron Microscopy (SEM) is a basic and fundamental tool in the study of geologic samples. The collision of a highly-accelerated electron beam with the atoms of a solid sample results in the production of several radiation types than can be detected and analysed by specific detectors, providing information of the chemistry and crystallography of the studied material. From this point of view, the chamber of a SEM can be considered as a laboratory where different experiments can be carried out. The application of SEM to geology, especially in the fields of mineralogy and petrology has been summarised by Reed (1996).The aim of this paper is to show some recent applications in the characterization of geologic materials.

1. Principle of the SEM

The SEM consists mainly of a column, a specimen chamber, a display and an operating device. The interior of the column is kept under high vacuum, and the electron beam produced by the electron gun is converged into a fine beam via electromagnetic lenses (condenser and objective lenses). By applying a scan signal to the deflection coils, the electron bean is scanned along the sample surface. The specimen chamber can be kept under high vacuum (conventional SEM) or under poor vacuum ("environmental" ESEM/"low vacuum" LV-SEM) conditions. As a result of electron-matter interaction, some signals are generated: secondary electrons, backscattered electrons, characteristic X-rays, cathodoluminescent light and others. The SEM utilizes these signals to form images.

Secondary electrons are produced near the sample surface and reflect the fine topographical structure of the sample. Backscattered electrons are those reflected upon striking the atoms composing the sample, and the number of these electrons is dependent on the composition (average atomic number, crystal orientation, etc.) of the sample. The primary (exciting) electrons may also be scattered inelastically by the sample's atoms, ejecting electrons of the inner-atomic shells and originating characteristic X-rays. In some types of samples, electron bombardment may raise bound electrons to higher energy levels, from which they return to their original states stimulating the emission of light by the process known as cathodoluminiscence (CL).

2. High resolution SEM (Field Emission Scanning Electron Microscope FESEM)

Secondary electrons are emitted from an extremely narrow area and carry information of the specimen surface. The spatial resolution of a SEM image is governed by the beam diameter which it depends on the emission source. In a Field Emission SEM (FESEM), the electron source consists of an extremely fine tungsten point from which electrons are drawn by a strong electric field. Nanometre resolution required for clay and whiskers crystals can be achieved by FESEMs. An example of a secondary electrons image obtained with a FESEM is given in Fig. 1.
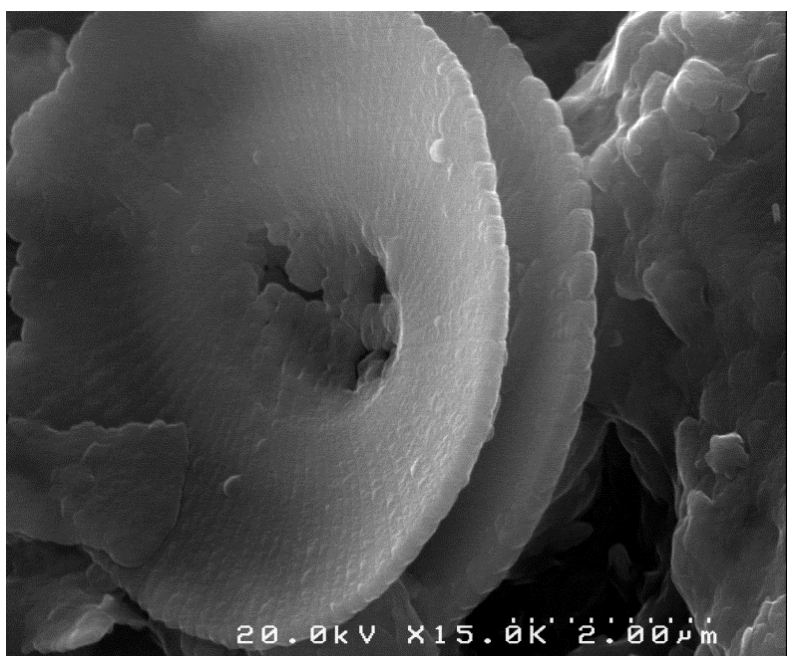

Figure 1: SEM micrograph of a calcareous nannoplankton (coccolithophore) in marine Miocene sediments of the Granada Basin obtained with a FESEM.

3. Chemical-contrast mineral identification (Backscattered electron images BSE)

The elastically scattered electrons having approximately the same energy as the incident electrons are collectively called as backscattered electrons (BSE) or reflected electrons. The probability that a primary electron is scattered elastically becomes larger as the mean atomic number (or electron density) of the specimen increases. Thus, backscattered electron signals provide rapid information about the compositional distribution of the specimen surface. BSE imaging in geological materials gives valuable information of petrographic textures and chemical zonation. Figure 2 shows a BSE micrograph of a zoned garnet crystal.
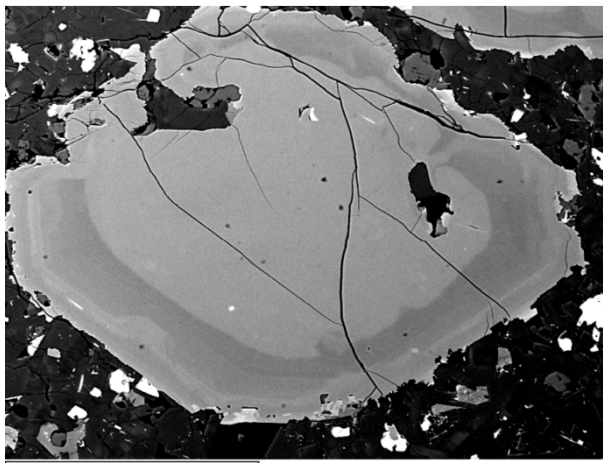
Figure 2: Chemical contrast with backscattered electrons of a garnet crystal.

## 4. Cathodoluminiscence images (CL-SEM)

Some minerals are inherently cathodoluminescent, but the intensity and colour of the light are often strongly influenced by defects in the crystal structure and by impurity atoms which behave as "activators" because they give rise to additional energy levels (Mn in calcite is a common example). Much geological CL work is done with an electron beam from a cold-cathode source coupled to an optical microscope. The use of a CL detector in a scanning electron microscope (CL-SEM) permits the generation CLimages of higher spatial resolution (Fig. 3).
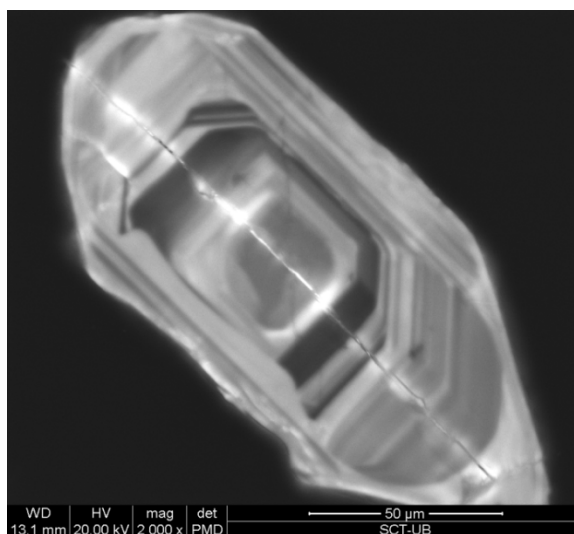
**Figure 3:** SEM-CL image of a zircon crystal.

5. X-ray analysis of fluid inclusions in salt (Cryo-SEM-EDS)

Direct access to brines trapped in old halite is possible by freezing and breaking halite crystals on a cooling stage inside a SEM (Fig. 4). Quantitative Energy Dispersive X-ray Spectroscopy (EDS) analyses of major solutes (Na, Mg, K, Ca, Cl and SO_4) in fluid inclusions can be obtained by comparing measured X-ray intensities with those obtained from liquid standard solutions with known composition (Ayora et al., 1994).
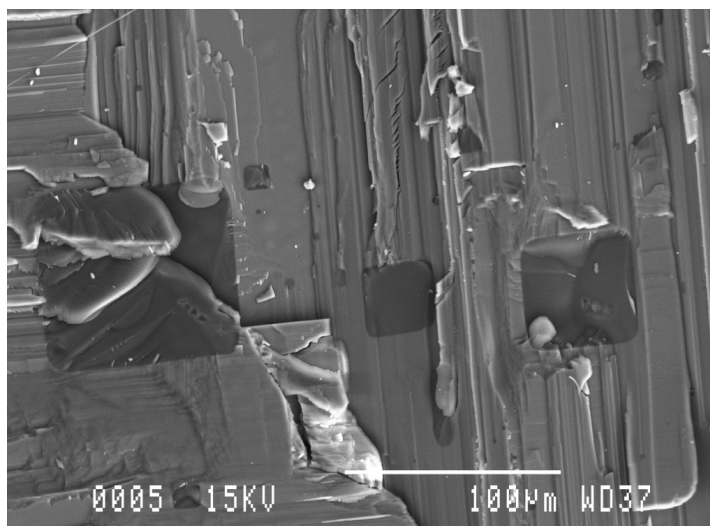
Figure 4: Secondary electron image of frozen fluid inclusions in a halite crystal.

The major ion composition of seawater varied through the geological time (Fig. 5). Fluid inclusion composition data obtained by Cryo-SEM-EDS from primary halite crystals in old marine evaporite deposits (Lowenstein et al., 2003) indicate that seawater had high Mg/Ca molar ratios (>2) and relatively elevated magnesium and sulphate concentrations during the Late Neoproterozoic, Permian, Triassic and the last 40 Ma. During Cambrian, Silurian, Devonian, Jurassic, and Cretaceous, seawater had relatively low Mg/ca ratios (<2) and Ca>SO_4. K concentrations have remained stable throughout Phanerozoic time.
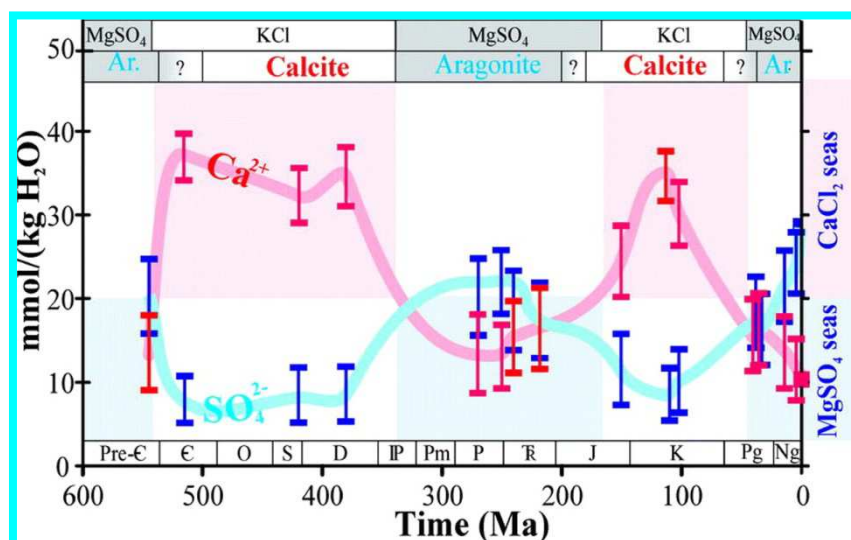
Figure 5: Secular variation in the Ca and SO_4 concentrations (in mmol/kg water) of seawater during Phanerozoic estimated from fluid inclusions in marine halites (Lowenstein et al., 2003).

6. Electron Backscatter Diffraction – *EBSD*

Electron backscatter diffraction (EBSD) is a SEM-based technique used for microstructure research, phase identification and also strain measurement. This technique relies on the interaction of the electron beam with the surface specimen. As a result of that, part of the primary electrons will be scattered within the sample in all directions. High-energy electrons which exit the specimen after one or more scattering events are named backscatter electrons (BSE) . Of these, the most useful for an EBSD analysis are the BSE which satisfy the Bragg equation for diffraction ($n\lambda = 2dsin\Theta$; Θ being the angle of incidence of the incident beam, *d* the interplanar spacing, λ the wavelength of the incident electron beam and *n* an integer) Under these conditions, they describe conical trajectories for each lattice plane and may be imaged on a phosphor screen as a diffraction lines called bands. A set of diffraction lines forms an electron backscatter diffraction pattern (EBSP) or Kikuchi pattern (Fig. 6).

Intersecting bands result in bright spots on the EBSP which correspond to zone axes, i.e. crystallographic directions. Thus elements of geometry can be recognized in EBSPs. In addition many electrons are inelastically scattered and contribute to the formation of a diffuse background in the pattern.

The resolution of EBSD is a function of the acceleration voltage, which controls the depth of penetration of the electrons in the specimen (interaction volume). The smaller the interaction volume is, the higher the resolution. Also, an angle of incidence of 70º between the electron beam and the specimen enhances the proportion of BSE able to be diffracted and escape from few tens of nanometers of these sample surface.

The quality of EBSPs is controlled by the beam current (or spot size). In order to obtain sharp EBSPs, a larger spot size will be required.

In non-conductive materials such as rocks and minerals, problems with the quality of the patterns and their resolution due to charging effects often appear. Next section explains how these problems can be solved.

6.1. Specimen preparation
Samples that are to be analysed by EBSD have to be crystalline. All minerals can be analysed although several minerals are challenging because of complex crystallography. Whole rock or minerals embedded in epoxy can also be investigated. If the aim of the study is the absolute orientation of crystals or structures, the sample should be oriented in space according to important directions such as lineation, foliation plane, etc.

The surface of interest must be smooth to avoid shadowing caused by topography. This can be achieved by mechanical polishing. During this polishing, an amorphous layer can be produced. This layer may be removed using chemo-mechanical polishing (colloid silica polishing). A large number of rock forming minerals can be chemo-mechanical polished successfully.

As we mentioned, insulating specimens will experience charge build-up under an electron beam. Coating the specimen with a conductive material such as carbon or gold removes that problem, but also reduces the quality of EBSP and orientation contrast images. EBSP quality can be increased by raising beam current, that is to say, increasing the spot size.

6.2. Applications of EBSD in mineralogy and geology.
Figure 7 shows some examples of typical analysis for a geological sample. From all the data obtained, one can examine the distributions of individual orientation measurements related to the microstructure (microtexture), the statistical distributions of orientations (the average texture of a bulk sample: macrotexture), and the misorientations between individual measurements (mesotexture).

(a)

(b)

(c)
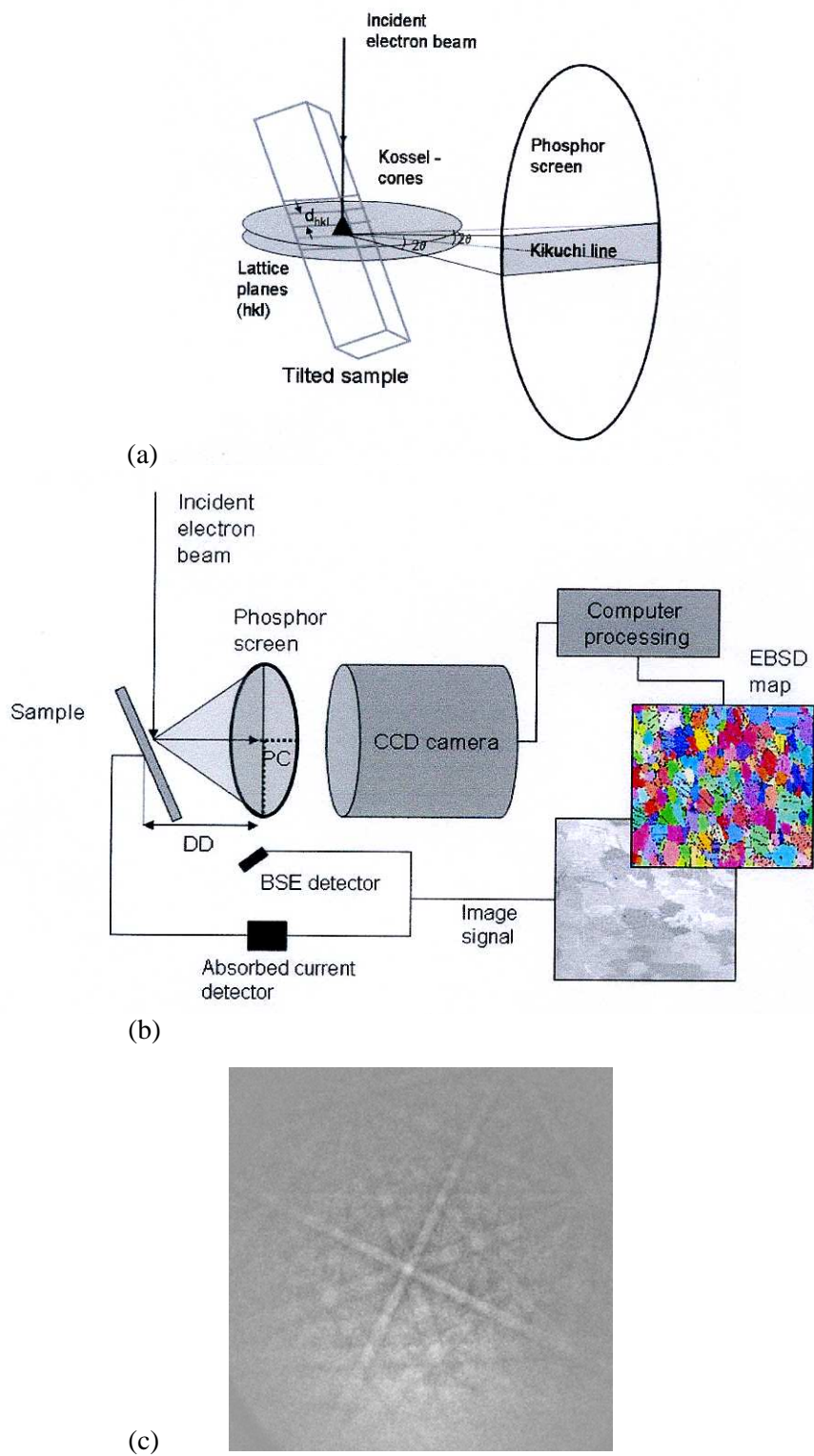
Figure 6: (a) Origin of Kikuchi lines from EBSD (adapted from Schwartz et al, 2000) (b) Typical EBSD hardware setup inside the SEM. (PC is pattern centre, DD is detector distance). (c) Example of a Kikuchi pattern for sphalerite. Acceleration voltage: 20kV.

All the measurements presented in this chapter have been made on a sphalerite (ZnS) sample from the Pyrenees region, specifically the Liat Mine. At each image point, we have calculated a value for the image quality (IQ) of the EBSPs (Fig. 7a). Inside grains, the IQ brightness depends on crystal orientation and is displayed in fairly bright grey levels, while along grain boundaries the IQ is low.

Misorientation distribution depends on mineral symmetry, which in this example is cubic, and it is plotted, most commonly, by means of inverse pole figures (Fig. 7b), as all the symmetrical equivalents will be plotted in the same place.

Pole figures (PF) are used to represent the texture of the analysed region. These kind of plots are useful to show when a sample is deformed following one direction, as we can see in Fig. 9, where a sharp texture (110) direction is represented.


(a)   (b)
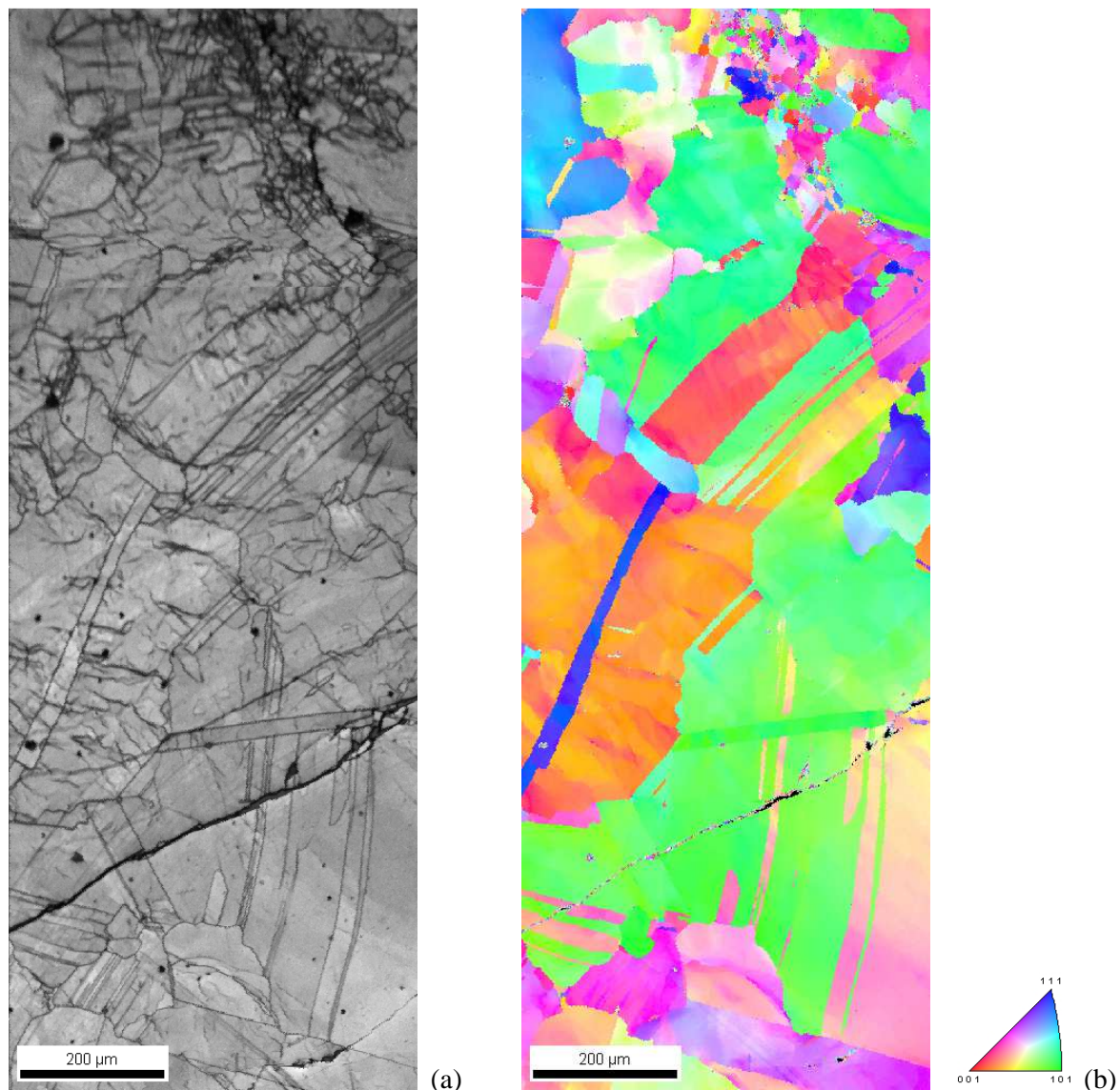
Figure 7: Examples of results from EBSD. The analyzed mineral was a sphalerite (ZnS) from the Liat Mine at the Pyrenees. (a) Image Quality map. (b) Inverse Pole Figure (IPF) map. General boundaries between grains could be defined (Fig. 8). In this figure, high-angle boundaries are shown in blue, whereas low angle boundaries (2 – 5º) are shown in red. These misorientation angles can also be represented in a chart.

MT.5
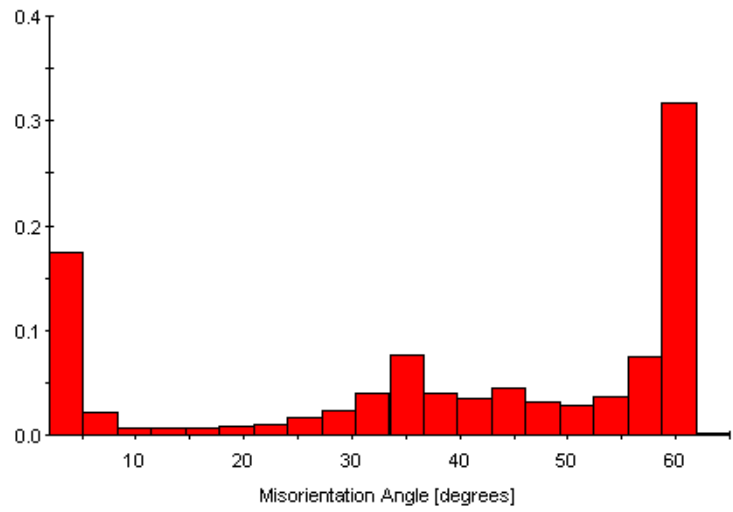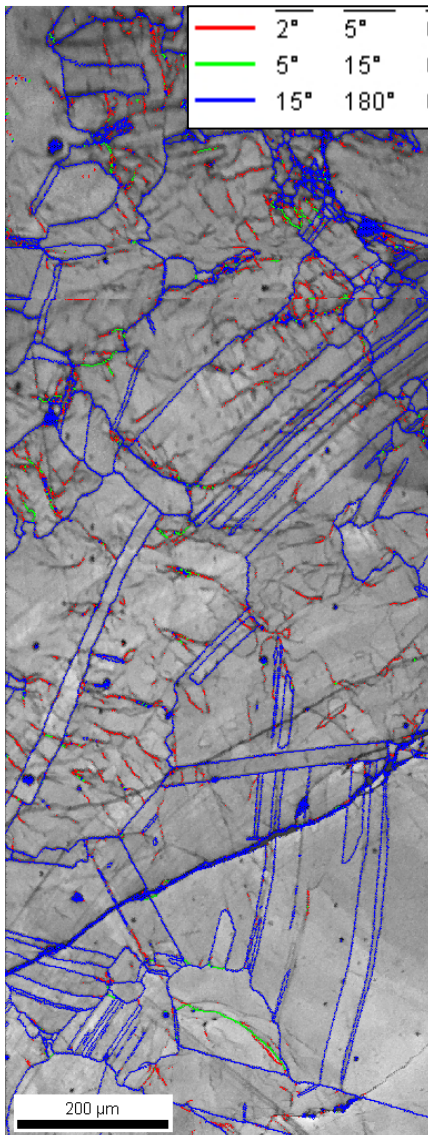
Figure 8: Grain Boundary map and misorientation chart corresponding to a sphalerite sample (ZnS) from the Liat Mine (Pyrenees)
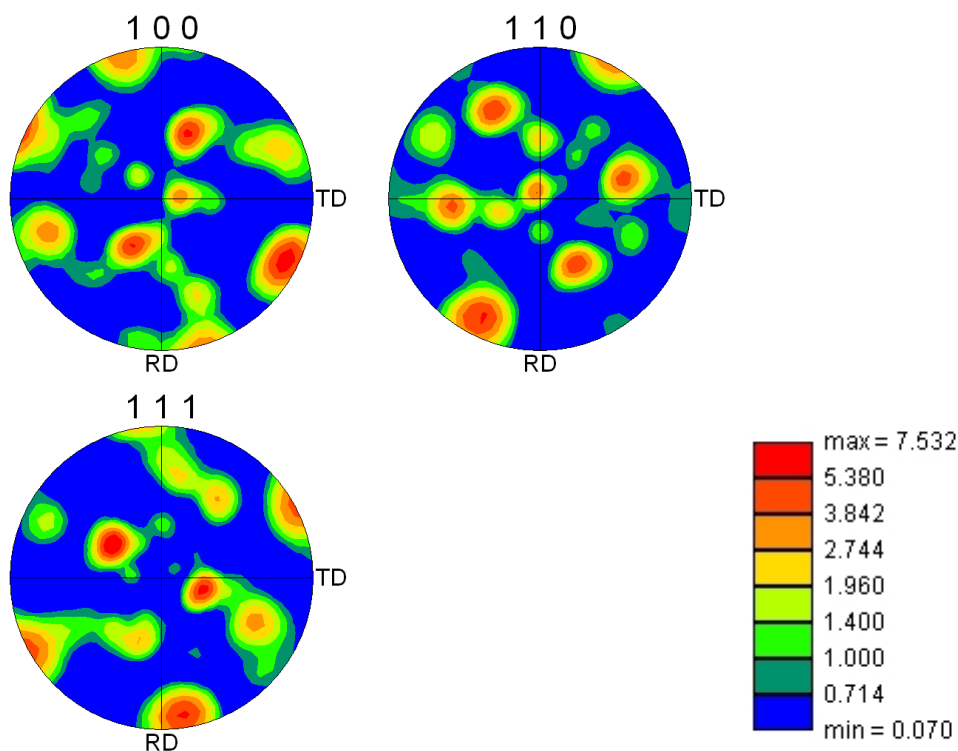
Figure 9: Pole figure for selected poles (100), (110) and (111) corresponding to a sphalerite sample (ZnS) from the Liat Mine (Pyrenees)

References

Ayora, C., García-Veigas, J., Pueyo, J.J., 1994. X-ray microanalysis of fluid inclusions and its aplication to the geochemical modeling of evaporite basins.

Lowenstein, T., Hardie L.A., Timofeeff, M.N., Demicco, R.V., 2003. Secular variation in seawater chemistry and the origin of calcium chloride basinal brines. Geology 31, 857-860.

Prior, D. J., Boyle, A.P. et al., 1999. The application of electron backscatter diffraction and orientation contrast imaging in the SEM to textural problems in rocks. Amer. Mineral., 84, 1741-1759.

Randle, V.,2002. Microtexture determination and its applications. London, The Institute of Materials.

Reed, S. J. B., 1996, Electron Microprobe Analysis and Scanning Electron Microscopy in Geology, Cambridge University Press

Schwartz, A. J., Kumar, M., and Adams, B. L., 2000. Electron backscatter diffraction in materials science : New York, Klumer Academic/Plenum Publishers.